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What was measured in Millikan’s study of the photoelectric effect?

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Millikan’s photoemission paper of 1916 is of great historical importance because it provided the first unambiguous experimental support for Einstein’s theory of the photoelectric effect. His graphical presentation of the results, for the correlation of stopping potential with frequency of the incident light on a sodium surface, is widely reproduced in textbooks, both at the high school and undergraduate levels. By far the most significant result that emerged from the experiments is the slope of this graph, which provided an accurate value of the Planck constant $h$. However, some modern textbooks also emphasize the intercept on Millikan’s graph, even though Millikan made little use of this. As previously emphasised, the intercept does not give a measure of the work function of the illuminated sample, but measures that of the collector surface. Millikan made this point very clear, and his experimental plots have been corrected for this, but it is still not generally realized that this is so. Even with Millikan’s correction, his intercept does not give the true work function for sodium. Neither of his surfaces was metallic, though this was assumed by Millikan and is assumed in textbook accounts. It is shown here that the sodium surface was almost certainly heavily contaminated with sodium hydroxide. The consequences for the interpretation of the experiment, and for the use of these results in teaching, are explored.

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I. INTRODUCTION

It is now a century since the appearance of the 1916 Millikan paper on photoemission, but it is still widely quoted and is available on the APS website as one of their “Featured in Physics” series. It is remarkable for several reasons, most notably for having been at least partly responsible for two Nobel Prizes. Millikan’s paper was the culmination of a decade of work, and it showed unequivocally and to great precision that many of the predictions that follow from Einstein’s analysis of the photoelectric effect were verified by his results. In particular, the slope of his graph provided by far the best estimate then available for the value of the Planck constant $h$. The experiment also provided very powerful evidence for the existence of photons. There is a remarkable irony in that, at least at the time, Millikan regarded the photon concept with considerable suspicion, and this concept became a cornerstone of quantum theory, which Einstein never accepted.

In the presentation speech at the award of the Nobel Prize to Einstein in 1921–1922 for his explanation of the photoelectric effect, the chairman of the awarding committee made it very clear that Millikan’s work had had a pivotal influence on their decision. The speech also emphasised the significance of the then revolutionary idea that radiation could have a particulate as well as a wave nature. Two years later, the Nobel Prize was awarded to Millikan. The citation mentions his work on electronic charge via the oil drop method he had to use, involving what was then state-of-the-art apparatus, have been superseded by equipment that is readily available and useable in the undergraduate or even the high-school laboratory. Consequently, experiments that claim to demonstrate the principles of Millikan’s work are now common in teaching laboratories. One purpose of this paper is to raise some queries about how this work is used for teaching. There is a common misunderstanding about what Millikan’s experiment does. Although Millikan’s own account is largely concerned with the results that follow from the slope of the graph, textbooks often give almost equal weight to the intercept. Furthermore, there is a longstanding puzzle about how Millikan was able to obtain stable measurement conditions for his experiments on the very reactive sodium surface, despite not having modern UHV techniques available. I intend to show that Millikan’s experiment is less simple than is implied both in his own account and in textbooks.

II. THE EXPERIMENT AS FREQUENTLY PRESENTED

In a number of textbooks, the Einstein equation for the energy of a photon,

$$E = hv,$$

is set out alongside a sketch of an apparatus similar to Fig. 1, where a metal sample in vacuo emits electrons when illuminated with monochromatic light. The current $A$ to a collector electrode is measured, and the repelling potential $V$ on this electrode is increased until no current flows. This is the critical stopping potential. Until quite recently, it was common to argue that this stopping potential, multiplied by the electron charge, is equal to the maximum kinetic energy of the electrons (in eV) leaving the sample. Thus, it was argued that the work function of the sample, or the minimum energy required to release an electron from the surface, can be determined from the difference between this energy and the photon energy. This is not true, and such a presentation has little connection with the real experiment.

A more sophisticated description indicates that the stopping potential experiment is done at several wavelengths, and that the slope of the line of stopping potential against...
frequency allows the Planck constant $h$ to be determined. This is a more accurate, though far from complete description of the Millikan experiment. However, it is frequently also stated, or implied, that the intercept of this line with the frequency axis, multiplied by $h$, is the work function of the sample. Both this argument and the corresponding one for the more rudimentary single frequency version are incorrect. This is not what the experiment determines.

III. WHICH WORK FUNCTION IS MEASURED?

The problem was clearly pointed out and analyzed by Millikan, who emphasized that there is another potential in the system, discussed below, which is being ignored in this wrong approach and which has a controlling influence on the stopping potential. The external current measuring system connects two metallic electrodes in vacuum, the illuminated sample plate or emitter, and the electron collector. Figure 2 shows a schematic energy-level diagram for two connected metals $M_1$ and $M_2$. The work function of $M_i(e\Phi_1)^2$ is the energy needed to raise an electron from the highest occupied energy level, the Fermi level $E_f$, to a position just outside the surface of the metal and with zero kinetic energy. This is the so-called “vacuum level” $E_{\text{vac}}$. Generally, the work functions of any two metals will be different, so when they are connected, electrons will flow from the metal which has the higher Fermi level to the other metal, until the two energies become equal.

Since the electron flow has generated local charges, the vacuum levels outside the two metals will be different, or, equivalently, there is a “contact potential difference” between these two metal samples. If the metal of the emitter in Fig. 1 is $M_1$, and that of the collector is $M_2$, then it is clear that in addition to the applied voltage $V$ there is an extra potential, corresponding to the contact potential difference of $(\Phi_2 - \Phi_1)$, which retards electrons travelling between the two plates if $\Phi_2 > \Phi_1$. Thus, this additional potential becomes part of the measured stopping potential. The result of this is that the intercept of the linear plot in the photoemission experiment measures not the work function of the sample material, but rather that of the collector. This point was explained clearly in Millikan’s papers, but was ignored in many textbooks. Forty years ago, this point was re-emphasised, first by James and then by Rudnick and Tannhauser in this Journal, who set out the argument in some detail, and gave many textbook examples of the problem. Shortly afterwards, this point was also made in a German language paper. In later editions of those textbooks cited by Rudnick and Tannhauser, either the mistake has been corrected or the text now relates only to the determination of $h$ from the slope of the plot. Nevertheless, the error concerning work function determination still persists in other textbooks and online.

IV. HISTORICAL NOTE ON THE CONTACT POTENTIAL PROBLEM

A referee has suggested that this common mistake of ignoring the contact potential difference between the collector and emitter when discussing photoemission might have had its origin in Einstein’s expression, given in his 1905 paper, for the maximum kinetic energy of a normally emitted photoelectron. In a present-day formulation, assuming reasonably low-energy electrons, this expression is

$$\frac{1}{2}mv^2 = h\nu - P,$$

where $P$ is Einstein’s symbol for the “Arbeit” (work) done by the excited electron in moving from the solid metal to the outside vacuum, equivalent to the work function labelled $e\Phi$ above. If this were all that had been presented in the offending texts, there would be no problem, but as discussed above these texts also assume that this kinetic energy can be measured simply by measuring the stopping potential, and they ignore the contact potential difference. It does not seem likely that this omission is directly connected with the above equation for the kinetic energy.

Nevertheless, it is worthwhile to look at exactly what Einstein wrote here. The formulation in the 1905 paper does not use the symbol “$h$” in the discussion of photoemission. This is probably for consistency with the rest of the paper, which explores other aspects of the quantization of light. In the German version below, I give what was printed in the 1905 paper, but in the somewhat free translations, I have changed this notation to a more conventional one.

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Fig. 1. An oversimplified illustration of Millikan’s photoemission experiment. Electrons are photo-ejected from a metal sample in vacuo, and an applied retarding voltage $V$ is varied until current $A$ at the collector electrode is zero.

Fig. 2. Energy levels for two different metals $M_1$ and $M_2$ in contact with each other. The work functions $e\Phi_1$ and $e\Phi_2$ have different values, so the vacuum level $E_{\text{vac}}$ immediately outside each sample changes accordingly. In Fig. 1, the contact potential difference $(\Phi_2 - \Phi_1)$ between collector and emitter is present as an additional voltage in series with the retarding potential $V$. 

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The relevant portion is

Die kinetische Energie solcher Elektronen ist

\[ R\beta \nu/N - P \]

Ist der Körper zum positiven Potential \( \Pi \) geladen und von Leitern vom Potential Null umgeben und ist \( \Pi \) eben imstande, einen Elektrizitätsverlust des Körpers zu verhindern, so muss sein:

\[ \Pi e = R\beta \nu/N - P \]

wobei \( e \) die elektrische Masse des Elektrons bedeutet.\(^{17}\)

The first two lines read

The kinetic energy of such electrons (i.e., those of maximum K.E. emitted normally) is

\[ h\nu - P \]

There is no possible doubt about this. However, Einstein continues:

“If the body (i.e., emitter) is charged to a positive potential \( \Pi \) and is surrounded by conductors at zero potential, and \( \Pi \) has a value just enough to prevent a current flowing from the body, then

\[ \Pi e = h\nu - P \]

where \( e \) is the charge on the electron,”

(The text continues with a version for one mole of electrons.)

Einstein’s implicit description of the circuit puts the emphasis on the current leaving the emitter, and on varying the emitter potential, with the collector at zero or reference potential. In contrast Millikan and later authors discuss the experiment in terms of varying the potential of the collector, referenced against that of the sample, until no electrons reach the collector. However there is no electrical difference between these two descriptions; each is increasing a retard- ing voltage until no current flows, as in Fig. 1 above.

Thus, in the second equation above, Einstein too is assuming that the product of the stopping potential \( \Pi \) with \( e \) can be equated to the kinetic energy, and has missed the point that his collector will also have a work function, so that as Millikan explained later (tactfully not mentioning the Einstein paper in this context), there is a contact potential difference between the two, as in Sec. III.

This is no discredit to Einstein. At this point in his paper, he is using the results of Lenard’s earlier experimental paper\(^ {18}\) for his comparisons, and in this paper Lenard claims that he is measuring electron velocities with his retarding potential, sometimes even referring to velocities in “volts.” His experimental arrangement was very similar to that of Fig. 1, with emitter and collector being a pair of parallel plates.\(^ {19}\) and Lenard measured both the current leaving the emitter and that arriving at the collector, as a function of applied voltage. Because of current loss to the walls, there was a considerable difference between these two measurements. In the paragraph quoted above, Einstein is actually proposing a substantial improvement to this experiment with his “surrounded by conductors”; this will prevent the current loss and it could almost be a specification for Millikan’s later Faraday cage collector (see Fig. 3 in Sec. V below for a schematic diagram). Three paragraphs later, he goes on to predict exactly the straight-line relationship that Millikan reported in the 1916 paper, even though, at the time Einstein was writing, there was virtually no experimental data that could support this idea.\(^ {20}\)

In that same year, Einstein published three other major papers, any one of which was worth a Nobel prize, at the same time as holding down a day job (so perhaps he can be allowed one minor slip). However, had they realized it, the authors of the various texts criticized earlier would have had a considerable authority for ignoring the contact potential difference in their descriptions of the experiment.

Finally, it is worth noting that Einstein was remarkably complimentary about Lenard’s work in his paper, calling it “bahnbrechend” (usually translated as “pioneering,” but the German has something of “trailblazing”). Despite this, Lenard later led a vicious campaign against Einstein that ultimately led to his expulsion from Nazi Germany. Einstein might have been amused that the minor slip noted above can be traced back to Lenard.

V. MILLIKAN’S METHOD OF CORRECTING FOR THE EXTRA POTENTIAL

Millikan set up his experiment so that he could measure separately both the stopping potentials at various photon energies and the contact potential difference between his sample and a reference electrode (of the same composition as his collector). The principle of his apparatus, though not the detail, is explained in Fig. 3. The entire apparatus could be exhausted to the limit of the vacuum pump (but see below and the Appendix). In the real experiment, the emitter was rotated between three stations.\(^ {21}\) The first of these (not shown) has a knife, which cuts a new surface, removing a thin shaving. The second is the photoemission position at the left of the diagram, where the light enters through a slit in the collector, which is in the form of a Faraday cage surrounding the emitter sample. During the photoemission experiment, this collector is connected as in Fig. 1.

![Fig. 3. A less simplified illustration of Millikan’s experiment. The collector electrode of Fig. 1 is a Faraday cage surrounding the emitter sample, and photons enter through a slit in this collector. The sample can be rotated from this photoemission station to another station in front of a reference electrode R of the same material (CuO) as the collector Faraday cage. Motion of R perpendicular to the sample (in the direction of the double-headed arrow) allows a measurement of the contact potential difference (see text) between the sample and R. A third station, omitted for clarity, allows thin shavings of the emitter to be removed, leaving an initially clean surface.](image-url)
In Fig. 3, the sample is shown rotated to the third station, at the top of the diagram. A reference electrode $R$ can be moved in to be very close to the emitter surface. These two surfaces, the sample and $R$, form a parallel-plate capacitor. When the external connection is made, this capacitor charges up to the contact potential difference $(\Phi_2 - \Phi_1)$. If, with zero applied voltage $V$, the reference electrode is rapidly dispensed away from the emitter, the capacitance will drop. The excess charge then flows through the ammeter (a sensitive mirror galvanometer in the real experiment) and this is detected as a current pulse. The voltage $V$ can now be varied until no current pulse is detected; this value of $V$ is the contact potential difference $(\Phi_2 - \Phi_0)$. This method is due to Kelvin, and is still used in modern surface science, though with considerable refinement.

The plots that Milikan reported were all adjusted for this contact potential difference, so that the intercept on his graph should apparently give the true work function of his sample. However, for the best experiments, using sodium, that were used for the very precise determination of $h$, Millikan’s intercept gives a value for the work function that is too small. The current best available value for the work function of sodium is 2.75 eV, and Millikan’s intercept is at 1.8(2) eV, less than that of any known metallic element. It appears that some present-day students are asked to plot out Millikan’s original data, because such exercises can be found in various course documents on the internet. The value of $h$ that Millikan calculated from the slope of his graph is within 1% of the currently accepted value, and if a modern value for the electron charge is substituted for Millikan’s, the discrepancy becomes less than 0.5%. It is odd that there should be such a gross discrepancy of the intercept, which is investigated below.

VI. THE COMPOSITION OF THE COLLECTOR AND EMITTER SURFACES

In the discussion so far, as also in the textbook accounts, it has been assumed that both the emitter and the collector are metallic surfaces. However, as we will see, in neither case is this true of Millikan’s experiment.

A. The collector surface

Both the collector electrode and the reference electrode for the measurement of the contact potential difference were made of copper. Probably because copper surfaces are rapidly attacked in air, Millikan chose to work with highly oxidized surfaces. This means that neither the collector nor the reference surfaces were metallic; in each case what faced the vacuum was the black semiconductor CuO.

B. The emitter surface

Milikan’s paper includes a detailed description of his experiment. He worked with freshly cut emitter surfaces in a glass vacuum system, and he had what was probably the most advanced vacuum pump then available, the Gaede “molecular pump,” a forerunner of the modern turbomolecular pump. He reports that his routine vacuum, achieved on a simple glass system, was “a ten-millionth of a millimeter” (i.e., $10^{-7}$ Torr or mbar), and that the ultimate pressure was lower than this, as measured by a sensitive McLeod gauge. He suggests at several points in the paper that there will be an appreciable attack on the sodium surface from residual oxygen, even at this low pressure. However, he makes no mention of the fact, which nowadays is very well known, that vacua in glass systems that are not extensively baked are seriously limited by very long term outgassing of adsorbed water from the walls. The McLeod gauge does not detect this water because it condenses when the residual gas is compressed. The true ultimate pressure in his system is then likely to have been around two orders of magnitude higher than his measurement and dominated by water vapour. (This is discussed further in the Appendix.) As is well known, water reacts very readily with sodium and the other alkali metals.

Milikan noted that his surfaces were rapidly contaminated, since the photoelectric yield decreased with time. Sometimes the contact potential difference shifted by as much as 2.5 V after the surface had been freshly cut, but he seems to have assumed that this was principally the result of attack by oxygen.

Remarkably, however, he found that for sodium he had a condition of stable and large photoelectric yield if he worked with a static pressure of $10^{-2}$ Torr. A fresh sodium surface was cut, and left until the photoelectric current was stable (“in an hour or so” (Ref. 14, p. 374)). The surface on which his best and most complete sets of measurements were made, and from which he calculated $h$, was studied “several hours” after cutting the surface. His surface, therefore, had reached some sort of saturation exposure to water, as well as being exposed to oxygen from the residual air.

The reactions of water vapor and oxygen with fresh sodium surfaces, prepared by evaporation in vacuo, have been examined in detail by using electron diffraction. Several results from these experiments are very relevant to Milikan’s experiment. When the clean sodium surface is exposed only to water, the characteristic diffraction lines of crystalline NaOH are observed, though the lines from the underlying Na metal are also visible. The intensity of these lines was constant over a series of exposures, which varied by a factor of 100 (thus there is a saturation effect, exactly as Millikan observed). The lowest of these exposures was 1 min at a water vapor pressure of $3 \times 10^{-4}$ Torr. This exposure would almost certainly have been exceeded during the several hours for which Milikan’s experiments were running. It therefore seems that Milikan and the electron diffraction workers had very similar chemical systems on their surfaces.

At the saturation exposure in the diffraction experiment, the lines from metallic sodium have a similar intensity to those from NaOH. The electron diffraction experiment has a sampling depth of the order of $10^{-6}$ cm, so the polycrystalline NaOH film at saturation is likely to have had a slightly smaller average thickness than this. Finally, when the surface is exposed to both oxygen and water, NaOH diffraction lines are seen, but none from Na$_2$O. Since both sets of experiments show that a saturation condition has been reached, these results give a very clear indication that Milikan’s experiments were actually on a sodium surface covered with an insulating film of crystalline NaOH, about $10^{-6}$ cm thick.

One difference between the two sets of experiments is that the Milikan setup had continuous exposure to water throughout the experiment, whereas the diffraction experiments were carried out in high vacuum, after the initial exposure. Sodium hydroxide picks up water very readily, so on the outside of Milikan’s relatively thick hydroxide film,
there would have been at least a monolayer of strongly adsorbed water and almost certainly other more weakly adsorbed layers of water molecules. Some evidence for this is provided by an experiment in which, after he had left the cut sodium surface for several hours in the static vacuum, he then turned on the vacuum pump, and found that the surface potential shifted rapidly by about 0.3 V. This is probably the result of pumping away weakly adsorbed water.

VII. EFFECTS OF THE SURFACE COMPOSITIONS ON THE MEASUREMENTS

A. The collector and reference electrodes

It is clear from Millikan’s text that the surfaces of both electrodes are semiconducting. However, this is not a serious problem for the reference electrode. So long as the collector and reference electrode have the same physical and chemical composition, measurement of the contact potential difference will provide the appropriate correction to the graphical intercept and would be expected to give a reliable work function for the emitter electrode.

Figure 4 shows a schematic of the energy levels of the vacuum/CuO semiconductor/Cu metal system. Here, $E_f$ is the Fermi level, VB is the top of the occupied CuO valence band, and CB is the bottom of the empty conduction band. The gap is about 1.2–1.7 eV, so at the scale of the diagram the vacuum level is above the top of the figure. Electrons arriving from the vacuum at the surface of the collector electrode (the left side of the diagram) will enter the conduction band of the CuO semiconductor. In reality, there are many conduction bands with various symmetries, but these all overlap and extend well above the vacuum level. Since the Fermi levels of oxide and metal are at equilibrium and the CuO bands bend down towards the interfacial region. Thus, there is no barrier at the interface, and any collected electrons will migrate to the empty states of the Cu metal electrode. As the potential of the collector electrode is raised against that of the emitter, so the vacuum level immediately outside the CuO surface rises, and electrons will cease to be collected when this vacuum potential brings the fastest of the photoelectrons to zero kinetic energy at this outer surface.

Thus, although Millikan’s instrument is constructed with semiconductor collector and reference electrodes, it will behave essentially as if these were metallic. The error in the work function measurement for sodium must have a different source.

B. The sodium emitter surface

We have seen above that the sodium emitter surface was almost certainly covered with a thin insulating film of sodium hydroxide. However, this would not stop all the photo-induced electrons from escaping to the vacuum. Electrons leaving the metal would have had a reasonably long mean free path in the NaOH film, since their energies would have been well within the band gap. For comparison, in various alkali halides, electrons of about 1 eV energy have escape probabilities of about 0.3–0.5 from a depth of $10^{-6}$ cm, the likely depth of the NaOH film.

In the determination of $h$, all that matters is that the slope of the line of stopping potential vs light frequency can be determined accurately. So as long as, for each photon energy, sufficient electrons at the maximum kinetic energy are leaving the film surface unscattered, the slope of the line will be unaffected by the presence of the insulator film.

Millikan had an independent check on the intercept values that he measured, since he also investigated the threshold for photoemission. Instead of using an electron retarding potential, in this experiment, an accelerating potential was applied to the collector so that all the emerging electrons were collected. The photon energy was then reduced until no photo-electrons were found. However, for this experiment, he did not have a continuously variable source of photons available. He had to use the emission lines of the mercury arc, which have fixed photon energies with substantial spectral gaps between them. Thus, Millikan could only determine whether or not emission occurred at these energies and had no information about intermediate energies. His experiment is therefore considerably less precise than the stopping potential determination. Nevertheless, within the accuracy of his determination, he reported good agreement between the results from this experiment and from the stopping-potential method. It appears, therefore, that despite the problems with the experiment mentioned above, his intercept gives a reasonably accurate value. The photoemission threshold energy. However, this threshold is not the work function of the sodium metal, the energy required to reach the vacuum level, because the electrons are not emitted into the vacuum but into the highly polar sodium hydroxide layer. Thus, it is not particularly surprising that the apparent work function of 1.8 eV is substantially different from the reported value of 2.75 eV for Na.

However, at first sight, it is rather surprising that the two methods do agree on the threshold energy. The photoemission threshold is the energy needed to inject electrons into the NaOH film and is independent of effects at the vacuum-NaOH film interface, since electrons are accelerated away from the outer interface in this experiment. However, the stopping potential method will be affected by any surface charges that build up at this interface. The sodium hydroxide layer is a bulk electron insulator and there is a flood of low energy (scattered) electrons present, so some surface charging would be expected. The fact that the methods do agree suggests that any such charges leak away. If, as seems likely, there are also multilayers of adsorbed water present, the
surface will be a very good proton conductor and some charge neutralisation may come from this. Also, those scattered electrons that have near-zero kinetic energy when they arrive at the outer surface will be solvated by the adsorbed water. These solvated electrons may be sufficiently mobile that they can reach a metallic region before decomposing (initially to H and OH$$^\text{-}$$), so this could also provide a path for charge neutralisation.

VIII. LITHIUM

Millikan’s paper reported similar experiments with lithium; however, it is difficult to make any comment about the nature of these surfaces because although lithium reacts readily with water it also reacts rapidly with nitrogen, particularly in the presence of water. Thus, the films on lithium are likely to have had a complicated chemistry. Nevertheless, because the slope of the graph gives good agreement with that for sodium, the film thickness was clearly small enough for some electrons to escape without major scattering. The measured threshold energy of 2.36 eV (for a fairly fresh surface) corresponds to escape into this film and not to the work function.

IX. CONCLUSIONS

A main conclusion here is that although Millikan had a brilliantly designed and constructed experimental setup, he was also quite fortunate to find a system that was both electrically stable over long periods and also allowed accurate measurements over a wide range of photon energies. Though his vacuum system was heavily contaminated by water vapor, which reacts rapidly with a sodium surface, after a certain amount of reaction, the resultant film of crystalline NaOH prevents, or at least greatly slows down, any further reaction. This gave him the stable condition for measurement in which the film happened to be sufficiently thin for a useable fraction of the photo-emitted electrons to escape unscattered. Under these conditions, he was able to get a remarkably accurate value for h. If the quasi-equilibrium film had been thicker, getting accurate results would have been much more difficult, since it would not then have been possible to obtain a stable condition for measurements. Without this circumstance, which led to very convincing results, the general acceptance of the quantized character of radiation might have been delayed for an even longer time after Einstein’s paper of 1905.

Millikan himself did not make much use of his intercept values in the 1916 paper, other than the cross-comparison with the direct photoelectric determination referred to above. The very different emphasis on the intercept of the graph in modern textbooks has probably arisen because equating this with the work function of the emitter seemed to be a simple concept that is easily taught. Unfortunately that concept is wrong. Reality is more complicated, and the true nature of what the experiment measures takes more time to explain even for the ideal case of truly metallic electrodes, since a measurement of the work function of the sample by this method also requires Millikan’s contact potential measurement. In the real system with which Millikan was working, with a NaOH overlayer, it simply was not possible for him to obtain a work function for the underlying sodium.

ACKNOWLEDGMENTS

I am indebted to Professor Brian Henderson, who brought some aspects of this problem to my attention many years ago, and I thank Professors Ignatius McGovern (Dublin) and Michael Ramsey (Graz) for careful readings of the text and for useful suggestions. Both referees have made substantial improvements to the presentation with their comments, and I thank them also.

APPENDIX: THE NATURE OF THE VACUUM IN MILLIKAN’S SYSTEM

After the initial pump-down, modern glass vacuum lines that are not baked reach a pressure of about 10$$^{-4}$$ Torr quickly, but may take an hour or more to get to 10$$^{-5}$$ Torr. Even with days of pumping, it is difficult to attain 10$$^{-6}$$ Torr, still an order of magnitude greater than Millikan’s claimed routine value of 10$$^{-7}$$. This is so even for lines constructed using wide bore (20+ mm inner diameter) tubing with relatively high molecular conductance. Judging from Millikan’s photograph of his setup, his connecting tube between the measurement cell and the pump had an internal diameter of less than 10 mm. The problem is not the pumping of air molecules, but the fact that atmospheric water adsors very strongly on glass surfaces (and also on the oxidized metal surfaces of present-day UHV systems) and desorbs quite slowly. Therefore, the true residual pressure, in any vacuum system that is not extensively baked at high temperatures, is dominated by water vapor from this desorption even when using a liquid nitrogen trap, which has a very high pumping speed for water vapor.

Millikan was using a McLeod gauge to measure his pressures, and because this compresses the gas being measured the water partial pressure is not detected in such a measurement (due to condensation of vapor). In relation to the McLeod gauge Millikan states, “Such a gauge gives, of course, no indication as to the amount of mercury vapor present.” It is very noticeable that here, and throughout the paper, there is no mention of water, even though the argument for water is almost the same as that for mercury vapor.

A referee has raised the very reasonable question of whether Millikan might have baked his system and an answer to this requires some more analysis of the equipment. The work reported in 1916 had been a more-or-less continuous project over the previous decade, and his apparatus had been evolving throughout this time. The final version, which he shows in Fig. 1 in the paper, is almost all-glass. This looks bakeable, but the quartz window that admits UV is sealed with “de Khotsinsky cement.” This softens around 100°C, which alone would place a severe limit on baking, but the potassium sample inside the apparatus would have melted at
the much lower temperature of 63.5°C. Thus, any baking could only have been up to 60°C and would have had to be done with extreme caution. Elsewhere, Millikan gives considerable experimental detail and it is almost inconceivable that if he had been carrying out such cautious baking he would not have mentioned it. The immediately preceding version of the apparatus, shown in Fig. 2 of Ref. 1, includes both a greased joint and a modified tap as part of the motion system for the reference electrode \( R \) (see Fig. 3), so this version could not be baked at all. The modification that eliminated the greased joints appears to have been made for the convenience of using an electromagnet for the motion of \( R \) rather than anything to do with vacuum quality. It therefore seems very unlikely that any baking at all was done, and that perhaps Millikan was unaware of the importance of water in limiting ultimate vacua. If pumped for a very long time, of the order of weeks, the water background would have diminished, but Millikan (and separately one of his students using an earlier form of the photoemission cell\(^{42}\)) reports only that pumping was continued until the McLeod gauges showed no or very low detectable pressures.

Around this time, detailed studies of the outgassing of water and other contaminants during the baking process were being made in some industrial laboratories\(^{43}\) driven by the need to have good vacua for light bulbs and radio and X-ray tubes. Langmuir reported particularly extensive work.\(^{44}\)

However, this work appeared after Millikan’s publication.

2. In Millikan’s paper, there is a long section at the end where he tries very hard to escape the obvious conclusions from his results; only later did he come to accept them (see Ref. 3).
4. Einstein’s law of the photo-electrical effect has been extremely rigorously tested by the American Millikan and his pupils and passed the test brilliantly.” S. Arhenius, Nobel Presentation Speech, December 1922. There are also indications in this speech that some of the doubt the Committee had about the more obvious reason for the award, the Theory of Relativity, arose because they were unsure whether this belonged more to Physics or to Philosophy. See *<http://www.nobelprize.org/nobel_prizes/physics/laureates/1921/press.html>*
5. A slightly more precise definition is given later in the paper. There is an extended discussion of the concept of work function and its history, with theoretical analyses, in S. Halas, “100 years of work function,” *Mater. Sci.* 24(4), 951–965 (2006).
7. The symbol \( \Phi \) is sometimes used for work function, so then it represents an energy. However, here \( \Phi \) is a potential, so the work function is the product of \( \Phi \) and the electron charge; this product is normally expressed in electron volts (eV).
8. Many laboratory demonstrations make use of photocells, which have the considerable advantage that the emitter surface has been prepared in a very good vacuum. Some such cells may give a correct value for the work function if, in the deposition of the volatile metal on to the emitter electrode, some has also been deposited on the collector, so that both electrode surfaces are of the same material; this is of course of no consequence in the normal use of the device.
15. This earlier notation is explained in the paper cited in Ref. 5.
16. A more literal translation of the entire paper is available at [http://einstein papers.press.princeton.edu/vol2-trans/114-].
17. The term “elektrische Masse” is rather strange; the literal translation gives “electric mass,” though from the context, it is clear that what is meant is what we would now call “electrical charge.” This may be a consequence of the language of atomic physics being in a state of flux, because the subject was only just being created, and Millikan’s oil-drop experiment was still six years in the future. Einstein’s “Masse” later became “Ladung.” (In technical German, “elektrische Masse” now means electrical charge!).
19. Lenard was carrying out a wide-ranging study of possible variables, including investigating whether or not there was any sort of field effect in photoemission and for this parallel plates were necessary.
20. It is sometimes claimed that Lenard did some sort of controlled photon energy variation. In fact, in the Lenard paper quoted by Einstein (Ref. 18), although there is a very good study of the effect of intensity of the light, this was for non-monochromatized light. There may be a hint of a photon energy effect in this paper, in that the stopping potential decreased slightly when the usual carbon arc source was replaced by a zinc arc, but Einstein does not mention this.
21. The rotating table actually carried three different samples mounted at different positions. These samples were the metals lithium, sodium, and potassium. No experiments were reported for potassium due to an unspecified accident and those for lithium were carried out after a new collector had been installed, so although in principle experiments might have been carried out on successive metals without breaking the vacuum, this was not the case in practice.
23. Kelvin probes can be found at, for example, [http://www_kelvinprobe.com/>.
25. With some justification, he refers to the apparatus as “a machine shop in vacuo.”
26. The values reported by Millikan and by other workers cited here are given in nm (Hg) or Torr, and for ease of comparison with the originals it seems better to maintain this unit; to the precision of the measurements, the unit is effectively the same as a millilob (100 Pa, 0.75 Torr).
29. The morphology of the film is unclear but it is unlikely to have had a uniform thickness.
30. In fact, Millikan found that a second collector electrode showed a slightly different potential from the first one, indicating a different position of the top of the valence band at the CuO surface, so the electrode preparation method does not give completely consistent results. However, any errors from this source are small compared with the discrepancy in the sodium work function.
33. Since the photons have been transmitted through the same surface film through which the electrons have to emerge, the band gap has to be greater than the energy of the photons, and therefore of the photoelectrons.

See, for example, <http://www.iaea.org/inis/collection/NCLCollectionStore/_Public/09/410/9410560.pdf>

Milletiian explains that he had to use the alkali metals, which have low photoemission thresholds, because these allowed him to work over a wide range of photon energies, and this allowed him to determine his line as accurately as possible. The experiment is severely limited by the fact that as soon as the photon energy exceeds the photoemission threshold of the collector electrode, measurements become very difficult, if not impossible, because light reflected from the sample generates a photoemission current from the collector. This collector emission causes severe interference when trying to find the zero of current for determination of the stopping potential, so Millikan needed to use the alkali metals in order to have as wide a range as possible of photon energies that were below this collector photoemission threshold. This was one of his many major improvements on the methods of earlier workers.

Millikan did report some experiments carried out as quickly as possible under dynamic vacuum conditions. Not surprisingly, the precision is lower and he was only able to measure one pair of points in each experiment; such results alone would not have been as convincing as several points on one line.


One such student exercise gives a work function of 2.3 eV from a graph that is claimed to be Millikan’s (Teaching of Advanced Physics project, UK Institute of Physics (high School level), item TAP 502-4 at <http://tap.iop.org/atoms/quantum/502/page_47014.html>). However, this has been arranged by presenting a graph where the straight line has been moved away from Millikan’s line. While this gives what may have been supposed to be the “correct” answer (see Ref. 24), the ethics of ascribing false data to an author are somewhat questionable.

These comments relate specifically to observations made using the system described briefly in P. J. Bassett and D. R. Lloyd, “Photoelectron spectra of halides I. Tetrafluorides and tetrachlorides of group IV,” J. Chem. Soc. A 1971, 641–645. More extensive work can be found in P. J. Bassett, Ph.D. thesis, University of Birmingham (UK, 1971), but they can probably be replicated on many other systems.


Gilley Gramme Machine

The 1916 catalogue of the L.E. Knott Apparatus Company of Boston notes that this is “a type of generator now generally used in large units for power and lighting stations, and lists it at $7.75. Although it represents an inefficient type of generator that is no longer used, the apparatus stayed in catalogues until at least 1950. This example is in the apparatus collection at the Williston Northampton School in Easthampton, Massachusetts. (Notes and photograph by Thomas B. Greenslade, Jr., Kenyon College.)